NASA-CR-193672

NAG 1-786

FINAL REPORT ON GRANT:

"DIAGNOSTIC STUDIES OF THE H_xO_y-N_xO_y-O_3 PHOTOCHEMICAL SYSTEM USING DATA FROM NASA GTE FIELD EXPEDITIONS"

P.I.: W.L. Chameides

School of Earth and Atmospheric Sciences

Georgia Institute of Technology

Atlanta, GA 30332

183577
P-6

The research effort supported in part by the subject grant focussed on three related topics. Our major effort was concentrated on the analysis of data gathered during GTE field expeditions. Ancillary efforts were directed at: the development and application of a Global Chemical Transport Model for the study of the atmospheric reactive nitrogen budget; the development and application of a one-dimensional, time dependent cloud model for the study of the impact of in-cloud aqueous-phase chemistry on the atmospheric sulfur budget; and mechanistic studies of the chemical processes involved in dry deposition of ozone to vegetative surfaces. In the sections below we briefly summarize the central conclusions of each of these efforts. These discussions are followed by a listing of the papers completed during the granting period and the graduate students supported by funds from the grant. Reprints and preprints of all papers completed with support from the grant are attached as Appendices.

1. Analysis of GTE-CITE I Data.

As a follow-up to our analysis of data collected during the Fall, 1983 GTE/CITE-1 expedition (Chameides et al., *J. Geophys. Res.*, **92**, 2131-2152, 1987), we carried out a study of the data gathered during the Spring, 1984 GTE/CITE-1 flights over the eastern North Pacific Ocean.

(NASA-CR-193672) DIAGNOSTIC STUDIES OF THE HxOy-NxOy-O3 PHOTOCHEMICAL SYSTEM USING DATA FROM NASA GTE FIELD EXPEDITIONS Final Report, 1 Jul. 1987 - 31 Jul. 1990 (Georgia Inst. of Tech.) 6 p
N94-13170
Unclas
G3/45 0180097

This data was statistically and diagnostically analyzed to identify the key processes affecting ozone and its precursors in the region. A complete discussion of our findings appeared in Chameides et al., *J. Geophys. Res.*, **94**, 9799-9808, 1989. The major conclusions of the study were: 1. In contrast to our previous findings for the Fall, 1983 flights (as well as previous modelling studies by a number of other investigators), photochemical reactions were found to represent a net sink for ozone in the middle free troposphere overlying the sampling region during the Spring, 1984 flights; 2. The ozone loss inferred from the Spring flights was caused by the lower average NO concentrations and higher average ozone concentrations implied by the Spring measurements; and 3. A detailed analysis of airborne NO measurements made during the GTE/CITE-1 flights by two independent chemiluminenscent instruments and a TP-LIF instrument indicate the existence of statistical (and possibly systematic) differences when NO concentrations are in the 10 - 20 pptv range. These differences make it difficult to characterize the effect of photochemistry on the ozone budget over the North Pacific Ocean with a high degree of confidence.

2. An Analysis of NO/NO_2 Ratios Observed During the NASA GTE/CITE-2 Field Expedition

As part of the Journal of Geophysical Research Special Issue on the GTE/CITE-2 Field Expedition, a study was carried out which compared observed and model-calculated NO_2/NO ratios in tropospheric air over the eastern North Pacific Ocean and the continental United States (Chameides et al., *J. Geophys. Res.*, **95**, 10235-10247, 1990). The major findings of our study were: 1. Large random variations are associated with NO_x measurements in remote locations making comparisons of NO_2/NO ratios from individual measurements statistically meaningless; 2. With the use of entire data sets spanning longer time-averages, statistically meaningful comparisons can be made, and these comparisons generally indicate reasonably good agreement between independently measured NO_2/NO ratios; 3. A comparison of observed and model-calculated ratios also indicated

reasonably good agreement but with a small but statistically significant discrepancy of about 25% (with a standard error of the mean of only 5%); and 4. The reasonable agreement between calculated and measured ratios provides strong evidence in support of the importance of peroxy radicals in the photochemical cycling of NO_x and the concomitant production of O_3 in the marine and continental troposphere.

3. An Analysis of Hydrocarbon Data Gathered During ABLE-2A

A diagnostic technique based on measured ambient concentrations and OH-reactivity has been developed to analyze detailed speciated hydrocarbon data and determine the key species involved in OH-scavenging and (if sufficient NO_x is present) O_3 production. This technique has been applied to the hydrocarbon data gathered during GTE/ABLE-2A field study in Brazil and other relevant data bases. It is anticipated that this study will be completed and submitted for publication this fall. Preliminary results indicate: 1. The tropical forests of Brazil generate large atmospheric abundances of reactive hydrocarbons through biogenic emissions - on a reactivity-based scale there is as much hydrocarbon in the forests of Brazil as in many urban centers in the United States, including portions of the Los Angeles Basin; 2. NO_x is limiting O_3 photochemical production over large portions of the lower troposphere.

4. Global Chemical Transport Model Studies

In a collaborative study with scientists at the Geophysical Fluid Dynamics Laboratory (GFDL), we have worked on the development and application of a 3-D Global Chemical transport Model for the study and simulation of the atmospheric cycle of reactive nitrogen. In a paper recently submitted for publication to the Journal of Atmospheric Chemistry (see attached preprint) we describe calculations designed to determine the role of stratospheric NO_y in the tropospheric

NO_y budget. The calculations differ from earlier GFDL simulations in that the model now uses improved schemes for rainout and washout as well as dry deposition and a simple algorithm for speciating NO_y into soluble and insoluble forms. While stratospheric injection is found to be an important mechanism for maintaining background NO_y levels in the middle and upper troposphere of mid-latitudes, the source cannot account for NO_y concentrations in the remote, lower troposphere and middle and upper troposphere in the tropics and sub-tropics. New simulations are underway to study the importance of biomass burning and lightning as reactive nitrogen sources.

5. Cloud Chemistry Studies

In order to study in-cloud, aqueous-phase chemical processes, a one-dimensional, time dependent model of a warm, precipitating, stratiform cloud was developed (Lin and Chameides, *J. Atmos. Chem.*, **10**, 1-26, 1990). This model was then used to investigate the effects of chemical inhomogeneity in cloud and raindrops on in-cloud chemistry. As described in the attached preprint (submitted to J. Atmos. Chem.,), we have found that chemical inhomogeneity can significantly enhance in-cloud SO_2 oxidation by reaction with dissolved O_3, effectively removing any limitation on sulfate production due to the lack of available H_2O_2. The results suggest that previous models, which almost universally assume a chemically homogeneous distribution of cloud and raindrops, have over-estimated the non-linearity of the in-cloud SO_2-oxidation pathway.

6. Dry Deposition Studies

In order to better understand the meteorological, chemical, and physiological processes responsible for ozone deposition to vegetation and its harmful effects, a theoretical model was developed to simulate the transfer of ozone from the ambient atmosphere, through the plant stomata, and into the cell-wall water. The calculations, described in Chameides, *Environ. Sci.*

Technol., **23**, 595-600, 1989, suggest that reactions in the mesophyllic cell walls with ascorbic acid (or a similar enzyme secreted by the cells) is the major sink of ozone depositing on vegetative surfaces during the daylight hours. In addition it appears that ascorbic acid might act to protect the plant from the harmful effects of ozone by preventing its penetration to the plasmalemma.

7. Publications

During the three-year grant period the following papers were published with partial support of NASA:

1. Acid dew and the role of chemistry in the dry deposition of reactive gases to wetted surfaces, W.L. Chameides, *J. Geophys. Res.*, **92**, 11,895-908, 1987.

2. Absorption cross sections and kinetic considerations of the IO species as determined by laser flash photolysis/laser-absorption spectroscopy, R.E. Stickel, A.J. Hynes, J.D. Bradshaw, W.L. Chameides and D.D. Davis, *J. Phys. Chem.*, **92**, 1862-1864, 1988.

3. High ozone events in Atlanta, Georgia, in 1983 and 1984, R.W. Lindsay and W.L. Chameides, *Environ. Sci. Technol.*, **22**, No. 4, 426-431, 1988.

4. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, W.L. Chameides, R.W. Lindsay, J.L. Richardson and C.S. Kiang, *Science*, **241**, 1473-1475, 1988.

5. Ozone precursors and ozone photochemistry over the eastern North Pacific Ocean during the spring of 1984 based on the NASA/CITE 1 airborne observations, W.L. Chameides, D.D. Davis, G.L. Gregory, G. Sachse and A.L. Torres, *J. Geophys. Res.*, **94**, 9799-9808, 1989.

6. Ozone trends in Atlanta, Georgia: Have emissions controls been effective? R.W. Lindsay, J.L. Richardson, W.L. Chameides, *JAPCA*, **39**, 40-43, 1989.

7. The chemistry of ozone deposition to plant leaves: The role of ascorbic acid, W.L. Chameides, *Environ. Science and Technol.*, **23**, 595-600, 1989.

8. Trace gases in the atmosphere of Mars: An indicator of microbial life, (J..S. Levine, C.P. Rinsland, W.L. Chameides, P.J. Boston, W.R. Cofer, III and P. Brimblecombe), reprinted from *The Case for Mars III: Strategies for Exploration - Technical*, **75**, ed. Carol Stoker, published by the AAS, 1989.

9. Model simulations of rainout and washout from a warm stratiform cloud, Lin Xing and W.L. Chameides, *J. Atmos. Chem.*, **10**, 1-26, 1990.

10. Airborne measurements of dimethylsulfide, sulfur dioxide, and aerosol ions over the southern ocean south of Australia, (H. Berresheim, M.O. Andreae, G.O. Ayers, R.W. Gillett, J.T. Merrill, V.J. Harris, and W.L. Chameides), *J. Atmos. Chem.*, **10**, 341-370, 1990.

11. Tropospheric Ozone: Formation and Fate (W.L. Chameides and J. Lodge), in *Ozone: Vegetation Effects*, Lewis Publishers, in review, 1989.

12. Observed and model-calculated NO_2/NO ratios in tropospheric air sampled during the NASA GTE/CITE II field study, (W.L. Chameides, D.D. Davis, J.D. Bradshaw, S. Sandholm, M.O. Rodgers, B. Baum, B. Ridley, M.A. Carroll, G.L. Gregory, H.I. Schiff, D.R. Hastie, A. Torres and E. Condon), *J. Geophys. Res.*, **95**, 10,235-10,247, 1990.

13. Natural hydrocarbons, urbanization, and urban ozone, (C.A. Cardelino and W.L. Chameides), *J. Geophys. Res.*, **95**, 13,971-13,979, 1990.

The following manuscripts have been submitted for review and publication:

14. Model studies of the impact of chemical inhomogeneity on SO_2 oxidation in warm stratiform clouds, (Lin Xing and W.L. Chameides), *J. Atmos. Chem.*, in review, 1990.

15. The relative impact of stratospheric production on tropospheric NO_y levels: A model study, (P.S. Kasibhatla, H. Levy II, J. Moxim and W.L. Chameides), *J. Atmos. Chem.*, in review, 1990.

8. Graduate Students

During the granting period the following graduate students have been supported in part with funds from the subject grant:

Jennifer Richardson	MS 1988
Lin Xing	Ph.D. 1990
Carlos Cardelino	Ph.D. candidate
Jiang Feng	Ph.D. candidate
William Hutzell	Ph.D. candidate
Ira Leifer	Ph.D. candidate